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(54) Bleaching of Cellulosic Material

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BLEACHING OF CELLULOSIC MATERIALS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates generally to improvements in processes for bleaching cellulosic materials in the form of pulp, such as wood pulp, and particularly to the rapid bleaching of pulps.

DESCRIPTION OF THE PRIOR ART

Pulping is the changing of wood chips or other lignocellulosic material to fibrous form. Chemical pulping requires cooking of such material in solution with a chemical in a "digester". The process includes partial removal of the coloring matter such as lignin associated with the wood.

Pulp, as it comes from the digester, whether produced from hard-wood or softwood or from non-woody materials, contains residual coloring matter. While unbleached pulp may be used for the manufacture of certain grades of paper, for example, heavy wrapping paper and paper for use in bags, pulp which is to be used for printing or paper or sanitary paper must be bleached.

Depending upon the nature of the raw pulp and the end use of which the pulp will be employed, various chemical bleaching stages and various sequences of these stages have been used heretofore. Among the principal chemical bleaching stages which have been used are the chlorination stage (designated "C"), the caustic extraction stage (designated "E"), the hypochlorite stage (designated "H"), and the chlorine dioxide stage (designated "D"). In addition, both chlorine and chlorine dioxide may be used in the same stage (designated "C_D") or ("D_C") and the chemicals may be used as a mixture or added sequentially. Various combinations of the above stages have been employed depending upon the specific conditions and bleaching requirements. For example, common bleaching sequences may include the following: CEH, CEHD, CEHED, CEHDED, and CEDED. Of these, the C_DEDED and C_DEHDED are the recognized standard sequences for producing 88+GE Brightness market pulp.

The C_DEDED sequence produces a high brightness pulp with a minimum of vicosity loss or cellulose degradation to the pulp. This results in a pulp which has high strength properties. The C_DEHDED sequence also produces high brightness, but heretofore the hypochlorite stage has caused degradation of the cellulose albeit in a controlled fashion. This results in some loss in paper strength, but the pulp requires less mechanical beating in order to develop its maximum strength, compared with pulp bleached by the C_DEDED sequence. The C_DEHED sequence is used to make the same type of pulp as the C_DEHDED sequence, but it has one fewer stage for control of brightness. The CEH sequence is used for semibleached pulp in the brightness range 65 to 75 GE Brightness Standard. The C_DEHD sequence has not normally been used for pulp requiring brightness greater than 86 GE because bleaching to higher brightness with this sequence generally results in a severe loss in viscosity and strength.

In the initial chlorination stage, chlorine is added to the washed pulp received from the digester. Ordinarily, the chlorination stage (C) is performed at temperatures in the range of about 30°C to 50°C, with a pulp consistency of about 3 percent. Under these conditions, the reaction time in the chlorination tower is about 30 to 60 minutes. The chlorine reacts directly with the lignin and other impurities in the pulp. Chlorine dioxide may be used in conjunction with chlorine (C_D) or in place of chlorine for the initial chlorination stage (D).

Following the chlorination stage, a caustic extraction stage (E) using a dilute aqueous solution of sodium hydroxide (0.5 to 5.0 percent NaOH based on oven-dry weight of pulp) is performed to dissolve the chlorinated and oxidized lignin as well as some of the resin. The extraction stage is usually performed at temperatures of about 50°C to 80°C for a period of about 60 to 120 minutes with a pulp consistency of 10 to 20 percent.

The next stage of bleaching is commonly a hypochlorite stage (H), although a chlorine dioxide stage is sometimes preferred. In the hypochlorite stage, either sodium hypochlorite (NaOCl) or

calcium hypochlorite ($Ca(OCl)_2$) is used to further oxidize the remaining lignin and other impurities in the pulp. Some degradation of the pulp as a result of shortening the chain length of the cellulose molecule usually occurs in the hypochlorite stage.

Following the hypochlorite stage, there may be a second alkaline or caustic extraction stage (E) or a chlorine dioxide stage (D).

SUMMARY OF THE INVENTION

The present invention provides an improved process for the delignification and bleaching of lignocellulosic material wherein the material is treated with chlorine dioxide (D) in combination with hypochlorite (H) in the presence of an acid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Bleaching is the treatment of cellulosic fibers to remove or alter the coloring matter associated with the fibers to allow the fiber to reflect white light more truly.

The present invention is concerned with the degradation of lignin and hence "delignification" and "bleaching" are used interchangeably.

Consistency is the weight of pulp fibers in a pulp suspension usually expressed as a percentage. For example, one pound oven dry fiber in one hundred pounds of a mixture of water and fibers would be a pulp suspension of 1% consistency. The consistency of the pulp will depend upon the type of dewatering equipment used.

One measure of the efficacy of a bleaching process is the degree of delignification. There are many methods of measuring the degree of delignification of the pulp, but most are variations of the permanganate test.

The permanganate test used herein provides a Permanganate number (KNO) a measure of potassium permanganate solution consumed by oven dry pulp under specified conditions. The Permanganate number is determined in accordance with TAPPI standard test method T 214 SU-71.

Brightness in the examples which follow was measured with an Elrepho (Trade Mark) brightness meter in accordance with TAPPI standard T217M. Viscosity measurements were made using a capillary viscometer method as outlined in TAPPI procedure T-230. The viscosity value (centipoise or "CPS") is useful to determine the degree of cellulose degradation during bleaching.

In the Tables, "oven dried" is abbreviated "OD", "hypochlorite" is abbreviated "hypo" and "centipoise" is abbreviated "cps".

The principles, features and advantages of the invention will be further understood upon consideration of the following specific examples.

Example 1

An 85 gram sample of unbleached Northern softwood kraft pulp having a Permanganate number of 17.5 was mixed with chlorine water at a charge level of 5.6% chlorine based on oven dry weight of the fibers in a closed glass bottle in a consistency of 3.5%. The bottle was immersed in a water bath maintained at 29°C for 45 minutes. After the retention, the chlorinated pulp was washed well with tap water on a vacuum drain Buchner funnel employing filter paper. The chlorinated pulp was then subjected to caustic extraction employing the following conditions: 2.5% NaOH based on oven dry pulp, 65.5°C, 90 minutes and 11% consistency. The extracted pulp was washed in the same manner described above for the chlorinated pulp. 5g of the chlorinated and caustic extracted pulp (CE pulp) was used for CEK number determination (the Permanganate number after the CE stage). The determined CEK number was 3.3 which was in the normal range practiced in a pulp mill (3.0-6.0). The remaining 80 grams of the CE pulp were equally divided into two 40 gram batches. The first batch was treated with chlorine dioxide alone as a control of first chlorine dioxide bleaching stage (called D_1 stage). The control D_1 bleaching was carried out under the following conditions: 1.1% ClO_2 charged based on OD pulp, 63°C, 150 minute retention time and 10% consistency. In this ClO_2 bleaching experiment the CE pulp mat was broken up in a Hobart

mixer with addition of the required amount of dilution water for consistency adjustment. The well broken-up pulp slurry was then transferred into a glass bottle, equipped with air-tight cap. Prior to addition of chlorine dioxide solution the pulp slurry in glass bottle was preheated to 57-63°C. The required amount of chlorine dioxide solution was added to the pre-heated pulp slurry in the bottle. Upon adding chlorine dioxide solution the bottle opening was closed immediately with an air-tight cap and was shaken vigorously to promote a thorough mixing between the chlorine dioxide solution and the pulp slurry. After said mixing the glass bottle was immersed in a water bath maintained at 63°C. At the end of the bleaching reaction, the pulp was checked for pH and residual chlorine dioxide and then washed with tap water in the same manner described before. A handsheet weighing 5 grams was prepared for brightness measurement of the D_1 stage. After air drying the sheet, the initial brightness was measured. The reverted brightness was read after aging the same sheet in a hot air circulating oven at 40.6°C for 60 minutes.

The second 40 grams of CE treated pulp mat was broken up in a Hobart mixer. Thereafter, 100ml of carbonic acid, which was prepared by saturating CO_2 gas into deionized water, was added while agitating. Immediately after the carbonic acid addition, a sodium hypochlorite solution was added at a charge level of 0.55% available chlorine based on oven dry weight of fiber with agitation. Upon the hypochlorite addition, the carbonic acid and hypochlorite mixed pulp slurry was transferred to a glass bottle equipped with an air-tight cap and preheated to 57-63°C. After the preheating, a chlorine dioxide solution was added at 50% of the charge level in the control bleaching, 0.55% ClO_2 based on ovendry weight of fiber in the pulp. The tightly closed glass bottle containing pulp fibers, carbonic acid, sodium hypochlorite and chlorine dioxide solution was immersed in a water bath maintained at 63°C for 90 minutes. The pulp consistency in the bottle was 10%, just like the control D_1 stage bleaching. The bleached pulp was washed and measured for brightness in the same manner of the first batch.

After the first chlorine dioxide bleaching, the two pulp samples were further subjected to the second caustic extraction (E_2) and second chlorine dioxide bleaching (D_2) under the same conditions as follows:

E_2 stage: 0.5% NaOH based on OD pulp
74°C, 60 minutes retention time
11% consistency

D_2 stage: 0.4% ClO_2 based on OD pulp
74°C, 200 minutes and 10% consistency

After the D_2 stage, initial and reverted pulp brightness and viscosity of the fully bleached pulp were measured.

The first batch thus was bleached in multi-stage bleaching sequence $CED_1E_2D_2$ and the second batch was bleached in multi-stage bleach sequence $CE(H+D)E_2D_2$. The chlorine dioxide bleaching with a combination of acid and sodium hypochlorite solution is referred to here as (H+D). The bleaching results of control CEDED and CE(H+D)ED bleaching are summarized in Table 1.

TABLE 1

	Batch 1	Batch 2
Bleaching Sequence	$CED_1E_2D_2$	$CE(H+D)E_2D_2$
D_1 or (H+D) Stage		
% ClO_2 on OD Pulp	1.1	0.55
% Hypochlorite on OD Pulp	0.0	0.55
% Substitution of Hypochlorite for ClO_2	0.0	50.0
% Total Available Chlorine Used	2.90	2.00
D_1 Stage Brightness Initial	81.1	81.2
Reverted	77.2	76.5
D_2 Stage Brightness Initial	88.6	88.4
Reverted	84.8	84.3
D_2 Pulp Viscosity (cps)	14.1	14.6

From the results shown in Table I, it is evident that sodium hypochlorite can be substituted for 50% of the ClO_2 normally used in the first chlorine dioxide stage in the multistage bleaching sequence CEDED. The chlorine dioxide bleaching with a combination of carbonic acid and hypochlorite gave the same brightness obtained with 100% chlorine dioxide in the first chlorine dioxide bleaching stage. Contrary to the teachings of the conventional chlorine dioxide and hypochlorite bleaching art, the addition of acid and hypochlorite at the high temperature did not cause the expected viscosity drop during the (H+D) bleaching.

In this example, one part by weight of hypochlorite replaced one part by weight of chlorine dioxide even though one part by weight of hypochlorite is equivalent to 0.38 part by weight of chlorine dioxide in terms of oxidizing equivalent. In this novel bleaching process, one part by weight of hypochlorite reacts like one part of chlorine dioxide in the presence of acid. The (H+D) bleaching therefore reduced the total available chlorine usage in the first chlorine dioxide bleaching stage from 2.9% to 2.0%, which was a 31% reduction.

Example 2

A 100 gram sample of unbleached Southern pine kraft pulp having a Permanganate number of 18.5 was treated, as described in Example I, with an aqueous solution of chlorine so that 5.94% chlorine was added based on the weight of the fibers. The chlorination treatment was carried out at a consistency of 2.8% for 30 min at 32°C. The chlorinated pulp was washed in the manner described in Example 1. The chlorinated pulp, at 3.5% consistency, was then treated with sodium hypochlorite solution and caustic soda solution for 20 minutes at 38°C. The hypochlorite solution was added at a charge level of 1.5% available chlorine based on oven dry weight of fiber, at the same time the caustic solution was added at a charge level of 2.0% NaOH based on oven dry weight of fiber.

The chlorinated and hypochlorite treated (CH) pulp was equally divided and one batch was bleached with chlorine dioxide alone as a control D_1 bleaching and the other was bleached with a

combination of carbonic acid and sodium hypochlorite and chlorine dioxide. The chemical charge level was 0.9% ClO_2 based on oven dry weight of fiber in the first batch and for the second batch sodium hypochlorite solution was added at a charge level of 0.45% which is 50% of the 0.9% ClO_2 added in the first batch, along with 60 cc carbonic acid solution and 0.45% ClO_2. The addition was made in the same manner as in Example 1.

After the D_1 bleaching for the first batch and the (H+D) bleaching for the second batch, air-dried brightness was measured for the two bleached samples. The two batches were then further treated with second caustic extraction stage with addition of sodium hypochlorite (E_H stage) and then with chlorine dioxide bleaching in the second D stage under the same conditions. The bleaching results on Southern pine kraft pulp are shown in Table II.

TABLE II

	$CHD_1E_HD_2$ Batch 1	$CH(H+D)E_HD_2$ Batch 2
D_1 or (H+D) Stage		
% ClO_2 on OD Pulp	0.9%	0.45
% Hypochlorite on OD Pulp	0.0	0.45
Volume of Carbonic Acid Added	0.0	60cc
D_1 Stage - End pH	3.3*	2.6
Brightness	71.2	71.3
Total Available Cl_2 Used (%)	2.37	1.63
D_2 Stage		
Initial Brightness	87.7	87.8
Reverted Brightness	82.4	83.0
Pulp Viscosity, cps	7.7	7.7

* 0.25% NaOH was added to the D_1 stage as pH buffer.

E_H conditions: 0.7% NaOH + 0.45% sodium hypochlorite, 71°C, 60 Min.

D_2 conditions: 0.4% ClO_2 on OD pulp, 74°C, 90 Min.

As the result in Table II shows, it is again evident that 50% of the chlorine dioxide used in the first dioxide bleaching stage can be replaced by hypochlorite at an equal weight basis without affecting the D_1 stage brightness as well as the final brightness after the D_2 stage in multistage bleaching process $CHD_1E_HD_2$. It is again demonstrated that addition of hypochlorite and acid did not cause any pulp viscosity drop. Example 2 also proves that the (H+D) bleaching is applicable whether the chlorinated pulp is treated with caustic extraction or with alkaline hypochlorite. It should be noted that the total available chlorine usage in the first chlorine dioxide bleaching stage was reduced by 31% in the (H+D) bleaching as compared to the control D_1 bleaching.

Example 3

The unbleached pulp employed in this example was Canadian softwood kraft pulp obtained from a mill located on the east coast of Canada. The Permanganate number of the unbleached pulp was 16.3.

After treating the pulp by chlorination with 4.63% Cl_2 at 2.8% consistency for 35 minutes at 38°C, the chlorinated pulp was then subjected to alkali/oxygen ($E/_O$) treatment in a modified laboratory pressurized reactor under the following conditions:

% NaOH	:	2.315% on OD weight of fiber
Consistency	:	15%
Retention Time	:	45 minutes
Temperature	:	74°C
O_2 Pressure	:	100 PSIG (7 Kg/cm^2)
pH In/Out	:	12.4/10.5
Permanganate number after CE/O	:	2.5

80 grams of the oxygen treated pulp sample was equally divided into two batches; one was treated with 0.9% ClO_2 (based on OD pulp) and the other was treated with 0.45% ClO_2 plus 0.45% sodium hypochlorite with addition of 50cc of carbonic acid. After the D_1 and the (H+D) bleaching, the pulp was further treated with caustic extraction and chlorine dioxide bleaching under the same conditions.

The results of bleaching sequences CE/ODED and CE/O(H+D)ED are shown in Table III.

TABLE III

Sequence	$CE/OD_1E_2D_2$	$CE/O(H+D)E_2D_2$
D_1 or (H+D) Stage		
% ClO_2 on OD Pulp	0.9	0.45
% Hypo on OD Pulp	0.0	0.45
Temperature (°C)	60	60
Time (Min.)	120	110
Consistency (%)	8	8
D_1 Brightness		
Initial	77.6	78.6
Total Available Chlorine(% Cl_2)	2.37	1.63
D_2 Stage		
Initial Brightness	87.2	87.8
Reverted Brightness	83.7	83.7

E_2 stage conditions: 0.35% NaOH on OD pulp, 71°C, 120 Min., 12% consistency

D_2 stage conditions: 0.2% ClO2 on OD pulp, 71°C, 165 Min., 10% consistency

From the results of Example 3 shown in Table III, it may be seen that in (H+D) bleaching the chlorine dioxide normally used after the E/O stage can be replaced to the extent of 50% with sodium hypochlorite at an equal weight basis. As compared to the D_1 bleaching the (H+D) bleaching even gave slightly higher initial

brightness after the D_1 and D_2 stage with the oxygen treated pulp with a 31% reduction of the available chlorine usage.

Example 4

A 175 gram sample of unbleached Southern pine kraft pulp having a Permanganate number of 16.3 was treated with 5.2% chlorine in the same manner as in Example 2. The chlorinated pulp was then neutralized with alkali for an extraction step at 3.5% consistency for 20 minutes at 38°C. The Permanganate number of the chlorinated and neutralized pulp (CN pulp) was determined to be 4.3. The CN pretreated pulp was equally divided into 5 batches for the first chlorine dioxide bleaching. In order to determine how much hypochlorite can substitute ClO_2 in the first chlorine dioxide bleaching stage, percent substitution level was increased from 0% (control), 20%, 50%, 70% and 100% (only hypochlorite). After the D_1 or (H+D) bleaching each pulp was further treated with alkali extraction with addition of caustic and hypochlorite (E_H) and chlorine dioxide bleaching (D_2) under the same manner described in Example 2. The bleaching results of increased percent substitution of hypochlorite in multi-stage bleaching process $CND_1E_HD_2$ are shown in Table IV. The changes in D_1 brightness and D_2 brightness and pulp viscosity by increasing the percent substitution are illustrated therein. As the table shows, a maximum substitution level is near 70% of the chlorine dioxide used in the control D_1 stage. Up to the 70% substitution neither final brightness nor pulp viscosity was adversely affected.

The Table IV also shows that chemical savings can increase as percent substitution increases, since at 1983 prices the cost of sodium hypochlorite is about 50% less as expensive as the cost of chlorine dioxide at an equal weight basis.

TABLE IV

EFFECTS OF SUBSTITUTION OF HYPOCHLORITE FOR CHLORINE DIOXIDE IN THE FIRST CHLORINE DIOXIDE BLEACHING STAGE IN CND_1E_HD2 BLEACHING OF SOUTHERN PINE KRAFT PULP

D1 or (H+D) STAGE

% Substitution of Hypo	0%	30%	50%	70%	100%
% Hypo	0	0.36	0.6	0.84	1.2
% CLO_2	1.2	0.84	0.6	0.36	0
Sat. CO_2 Water	0.0	40cc	80cc	120cc	160cc
Temp., °C	57	57	57	57	57
Time, Min.	90	90	90	60	35
% Consistency	8	8	8	8	8
E_H Stage % NaOH	0.75	0.75	0.75	0.75	0.75
% NaOH	0.50	0.5	0.5	0.5	0.5
D_2 Stage, % ClO_2	0.4	0.4	0.4	0.4	0.4
CN KNO	4.3	4.3	4.3	4.3	4.3
D_1 Brightness					
(Initial)	66.3	68.9	68.9	66.4	70.8
(% Residual)	(0.15)	(0.11)	(0.06)	(0.0)	(0.0)
D_2 Brightness					
Initial	86.9	87.8	87.9	87.2	86.7
Reverted	83.3	83.6	83.1	82.4	82.0
(% Residual)	(0.102)	(0.083)	(0.085)	(0.072)	(0.073)
D_2 Viscosity (CPS)	8.0	8.6	8.3	8.3	6.2
Total Avail. CL_2 Charged (%)	9.903	9.3	8.93	8.54	7.85
Total Avail. CL_2 Consumed (%)	9.251	8.81	8.55	8.29	7.76

EXAMPLE 5

The Northern softwood kraft pulp used in Example 1 was treated with chlorination and caustic extraction under the following conditions:

C stage: 5.2% chlorine based on OD pulp
3.5% consistency, 29°C and 45 minutes

E stage: 2.5% NaOH based on OD pulp
10% consistency, 65.5°C and 90 minutes

CE-Permanganate number = 4.3

The CE pulp was equally divided into three batches. The first batch was treated with only chlorine dioxide at 1.1% ClO_2 charge level based on oven dried pulp as a control first chlorine dioxide bleaching. The second batch was treated with the (H+D) bleaching with addition of carbonic acid at chemical charge levels of 0.55% ClO_2 and 0.55% hypochlorite (50% substitution level). The third batch was treated with the (H+D) bleaching without addition of carbonic acid. All three batch bleachings were carried out in 8% consistency at 63°C. When hypochlorite was added to chlorine dioxide, the retention time had to be shortened from 180 minutes to 60 minutes because the addition of acid and hypochlorite accelerated chlorine dioxide bleaching reaction. The three batches were further treated with the second caustic extraction and the second chlorine dioxide bleaching as in Example 1. The results of this experiment are given in Table V.

Comparing the result of batch 1 with that of batch 2, the 50% substitution of hypochlorite for chlorine dioxide with addition of carbonic acid gave higher reverted brightness of the resulting pulp, indicating the (H+D) bleaching improved the brightness stability. As the final brightness and viscosity of the batch 3 are compared with those of batch 2, without the acid addition, the resulting pulp will have lower reverted brightness, less stable brightness and lower pulp viscosity indicating some cellulose degradation during the (H+D) bleaching. From the results, it is

evident that the acid addition is required to prevent the pulp viscosity loss and to improve the brightness stability in the (H+D) bleaching process.

Table V

EFFECTS OF CARBONIC ACID ADDITION
NORTHEASTERN SOFTWOOD KRAFT PULP

	Batch 1 D_1	Batch 2 (H+D)	Batch 3 (H+D)
	1.1% ClO_2	180cc Carbonic Acid	180cc tap water
		0.55% hypo 0.55% ClO_2	0.55% hypo 0.55% ClO_2
Temp. (°C)	63	63	63
Time (Min.)	180	60	60
Consistency (%)	8	8	8
E_2, % NaoH	0.5	0.5	0.5
D_2, % ClO_2	0.35	0.35	0.35
D_2 Bright.			
Initial	87.2	87.5	87.6
Reverted	83.0	84.4	83.5
D_2 Viscosity, cps	18.7	18.9	17.2

EXAMPLE 6

The CE prebleached pulp was prepared from the Northern softwood kraft pulp as discussed in Example 1. The CE pulp prepared was equally divided into three batches for the (H+D) bleaching followed by E_2 and D_2 bleaching. The first batch was treated with carbonic acid and 0.55% hypochlorite followed by 0.55% ClO_2. The

second batch was treated with the same amount of hypochlorite and chlorine dioxide but without addition of carbonic acid. The third batch was first treated with a 0.55% ClO_2 for 120 minutes at reaction temperature of 63°C and, at the end of the ClO_2 reaction, 0.55% hypochlorite was injected with carbonic acid. After a few minutes of retention at 63°C the chlorine dioxide and hypochlorite bleached (D+H) pulp was washed. The results of these bleaching experiments are shown in Table VI.

As may be seen from a comparison of the result of batch 1 with that of batch 2, it is again evident that without carbonic acid, the reverted brightness suffered as shown in Example 5. The result of batch 3 indicates that in this novel bleaching process the addition of hypochlorite and acid can be reversed; instead of the addition prior to ClO_2 addition the hypochlorite and acid can be added at the end of ClO_2 bleaching reaction in the same bleaching stage. The reverse addition may improve further the final brightness of the resulting pulp as shown in the Table VI.

TABLE VI

Mode of Treatment Sequence	(H+D) Batch 1	(H+D) Batch 2	(D+H) Batch 3
	1. Carbonic Acid and 0.55% hypo	1. No carbonic acid 0.55% hypo	1. 0.55% ClO_2
	2. 0.55% ClO_2	2. 0.55% ClO_2	2. 2 hours reaction at 63°C
			3. 0.55% hypo and carbonic acid
	E_2 (0.5% NaOH) D_2 (0.4% ClO_2)	E_2 (0.5% NaOH) D_2 (0.4% ClO_2)	E_2 (0.5% NaOH) D_2 (0.4% ClO_2)
Brightness			
D_1 (Initial)	76.4	75.6	75.9
D_2 (Initial)	89.1	88.9	90.3
(Reverted)	86.8	82.8	87.0

EXAMPLE 7

In this example, different modes of addition of carbonic acid/hypochlorite/ClO_2 solution in the (H+D) bleaching stage were evaluated. Four different modes were evaluated:

Mode 1. Simultaneous addition of carbonic acid and hypochlorite solution followed by 30 minutes retention at room temperature and then addition of ClO_2 solu-

tion without washing step after the hypochlorite addition and retention.

Mode 2. The same mode of addition as Mode 1 but with a washing step prior to the ClO_2 addition.

Mode 3. Simultaneous addition of carbonic acid and hypochlorite solution and ClO_2 solution while agitating.

Mode 4. Sequential addition of carbonic acid first and hypochlorite solution and ClO_2 solution last without retention time and washing between each addition.

The CE pulp sample was prepared by the same manner as in Example 1.

All four (H+D) bleaching experiments were carried out at 63°C in 10% consistency but with varying retention times. The effects of different addition modes were monitored by reading initial and reverted brightness of the resulting pulp after the (H+D) stage. The results are shown in Table VII. From the result, it is obvious that this novel bleaching with a combination of hypochlorite and chlorine dioxide does not require retention in time or heating and washing step between the hypochlorite addition and chlorine dioxide addition, and that the addition of acid, hypochlorite and chlorine dioxide solutions can be added simultaneously or sequentially. However, the sequential addition may be more effective than the simultaneous addition.

Mode of Addition 1	2	3	4
- Carbonic Acid + hypo (simult.) - 30 minutes retention at room temp. - No washing - ClO_2 addition	- Carbonic Acid + hypo - 30 minutes retention - Washing - ClO_2 addition	Simultaneous addition of carbonic acid/ hypo/ClO_2	Sequential addition (Carbonic acid) - Hypochlorite-ClO_2) - no retention and washing after hypo
Final pH			
2.0	2.3	2.5	2.3
ClO_2 Residual (titre) 0.3cc	0.2cc	0.3cc	0.3cc
Ret. time in (H+D) stage 120 min.	120 min.	80 min.	90 min.
(H+D) Brightness Initial			
76.6	75.1	74.1	75.2
Reverted			
73.2	72.6	71.5	72.6

EXAMPLE 8

A CE prebleached pulp was prepared in the same manner described in Example 5 for Northern softwood kraft pulp. The CE pulp was equally divided into three batches for the first chlorine

dioxide bleaching stage in multistage bleaching CED_1ED_2. The first batch was bleached with chlorine dioxide only at a charge level of 1.1% ClO_2 based on OD pulp at 63°C for 180 minutes. The second batch was bleached with a combination of carbonic acid and hypochlorite and chlorine dioxide at a 50% substitution of hypochlorite for chlorine dioxide (0.55% hypochlorite plus 0.55% ClO_2) at the same temperature of the first batch but with reduced retention time due to its faster bleaching reaction. The third batch was treated with the same chemical level of the second batch but at lowered temperatures. The dioxide bleaching temperature was lowered from 63°C to 54°C. After the D_1 or (H+D) bleaching those batches of pulp were further treated in the E_2 and D_2 stage by the same manner in Example 1. The result of lowered temperature in the (H+D) stage is shown in Table VIII. From the result it is obvious that in this novel (H+D) bleaching the bleaching temperature can be lowered by 9°C from 63°C to 54°C without adversely affecting the final brightness of the resulting pulp of multistage bleaching $CE(H+D)E_2D_2$.

TABLE VIII

Northern Softwood Kraft Pulp

CE pulp ($CEKn_o$ 4.2)

D_1 or (H+D)	Batch 1 (Control)	Batch 2 (H+D)	Batch 3 (H+D)
% ClO_2	1.1	0.55	0.55
% Hypo	0.0	0.55	0.55
Temp. °C	63	63	54
Retention time (Min)	180	120	150
Residual, titre (ml)	1.0	none	none
pH	1.7	2.4	2.6
E_2, % NaoH	0.5	0.5	0.5
D_2, % ClO_2	0.4	0.4	0.4
Brightness			
D_1 (Initial)	77.6	72.1	73.1
D_2 initial	90.1	90.1	90.1
D_2 reverted	85.6	85.5	85.4

EXAMPLE 9

Effects of different temperature of the (H+D) stage were again investigated in the multistage bleaching process $CN(H+D)E_HD_2$ using Southern pine kraft pulp. A chlorinated and alkali neutralized pulp was prepared by the same manner in Example 4. The K number of the CN pulp was 5.2. The CN pulp was equally divided into four batches. Each batch was bleached with the (H+D) bleaching at different temperatures, 48°C, 54°C, 60°C and 71°C. After the (H+D) bleaching, all three pulps were further treated with second caustic extraction with hypochlorite (E_H) and second chlorine

dioxide bleaching under the same conditions. The results are shown in Table IX. From the result, it is again evident that in the novel (H+D) bleaching, its bleaching termperature can be lowered to 48°C without any adverse effect on the final brightness and pulp viscosity from the normal temperature range of first chlorine dioxide bleaching, 60°C - 71°C. The lowering of bleaching temperature means a substantial energy savings at the bleach plant.

TABLE IX

	Batch 1	Batch 2	Batch 3	Batch 4
Temperature in (H+D) Stage, °C	48	54	60	71
Retention time, min.	180	120	100	80
Consistency, %	8	8	8	8
End pH in (H+D)	2.25	2.25	2.2	2.1
% Residual in (H+D)	0.0	0.0	0.0	0.0
(H+D) Brightness (Initial)	73.2	70.1	71.8	73.2
D_2 Brightness,				
Initial	87.9	87.4	87.9	88.3
Reverted	84.3	83.9	84.0	84.9
D_2 Viscosity, cps	13.3	14.0	13.5	13.7

EXAMPLE 10

Using a Northern softwood kraft pulp the CE prebleached pulp sample was prepared under the following conditions:

C stage: 5.2% chlorine based on OD pulp,

3.5% consistency, 29°C and 45 minutes

E stage: 2.5% NaOH based on OD pulp,

11% consistency, 71°C and 90 minutes

The prepared CE pulp was equally divided into six batches for the $(H+D)E_2D_2$ bleaching using six different acids in the (H+D) bleaching stage. The six different acids evaluated are carbonic acid (saturated CO_2 water), acetic acid (10% concentration), nitric acid (10%); hydrochloric acid (1N solution), sulfuric acid (4N solution) and phosphoric acid (10% solution). Each acid was added in an amount which pH of the (H+D) bleaching reached in the range of 2.0-2.5. The temperature and retention time were held constant at 57°C and 60 minutes respectively. After the (H+D) bleaching each pulp was further treated with 0.5% NaOH in E_2 stage and 0.35% ClO_2 in D_2 stage under the same conditions described in Example 1. The results of different acids are given in Table X. From the results shown it is obvious that in the noble (H+D) bleaching process besides carbonic acid other organic and inorganic acid can be used as long as the end pH reaches in the range of 2.0-2.5. Regardless of the acid used, the same final brightness can be achieved without affecting pulp viscosity.

However, considering practical application of this novel (H+D) bleaching process under mill environments, weak acids having ionization constant of 4-7 are preferred such as acetic acid, phosphoric acid and carbonic acid in order to avoid any danger of acid cellulose degradation in case of overfeeding strong acids such as sulfuric, nitric and hydrochloric acids. Among the weak acids evaluated, carbonic acid is preferred since it has the following advantages over other acids:

1. Carbonic acid can be readily prepared at the mill by injecting CO_2 gas into mill water.
2. It does not impose corrosion problems related to chloride and sulfate ions.
3. It does not impose any hazard in working environments because CO_2 gas is not toxic.

4. Any overfeeding will not cause an undue cellulose degradation.
5. It may be less expensive than other acids in neutralizing or acidifying alkaline pulp slurry.

TABLE X

Bleaching Sequence: $CE_1(H+D)E_2D_2$

Acid	End pH of (H+D) Stage	(H+D) Brightness	D_2 Brightness	D_2 Viscosity (cps)
Carbonic	2.45	69.1	88.3/84.7	20.4
Acetic	2.50	68.8	88.1/84.3	20.5
Nitric	2.30	69.3	88.5/84.5	21.1
Hydrochloric	2.30	68.5	87.9/84.0	21.2
Sulfuric	2.25	68.7	88.7/84.8	20.4
Phosphoric	2.30	68.5	88.7/84.9	20.7

It is apparent that other variations and modifications may be made without departing from the present invention. Accordingly, it should be understood that the forms of the present invention described above are illustrative only and not intended to limit the scope of the invention as defined by the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the delignification and bleaching of lignocellulosic material the improvement which comprises the step of treating said material with chlorine dioxide in combination with hypochlorite in the presence of an acid, the end pH of the process being from 2.0 to 2.5.

2. The method in accordance with claim 1 wherein the chlorine dioxide treatment is carried out prior to the addition of hypochlorite.

3. The method in accordance with claim 1 wherein the hypochlorite treatment precedes the addition of chlorine dioxide.

4. The method in accordance with claim 1 wherein the acid is taken from the group consisting of carbonic, acetic, nitric, hydrochloric, sulfuric and phosphoric.

5. The method in accordance with claim 4 wherein the acid is carbonic acid.

6. The method in accordance with claim 1 wherein the treatment is carried out at a temperature between 48°C and 60°C.